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The application of a modified MacMichael viscometer in rheologic studies of montmorillonite clays

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THE APPLICATION OF A MODIFIED MACMICHAEL VISCOMETER IN RHEOLOGIC STUDIES OF MONTMORILLONITE CLAYS

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Master of Science

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by

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PREFACE

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B.E.F.

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C H A P T E R I

INTRODUCTION

Available instruments for viscosity and rheologic measurements necessitate disruption of the system under test prior to observation. Generally, the gel structure of a thixotropic clay must be disturbed by shaking, pouring into a container for testing, and again upon insertion into the sample of the bob, spindle or paddle of the instrument. Also, these instruments yield a single point reading which is only a final or average value, depending upon the instrument. The occurences during the test itself cannot be observed. Accordingly, it seemed feasible to determine, if possible, what other rheologic factors are involved in the breakdown of the gel structure of a thixotropic clay dispersion.

The objective of the study was to design and test an instrument which would not require disturbing the sample before testing, which would give minimal destruction of the sample upon entry of the test probe into the sample, and which would give complete permanent recordings throughout the time of testing.

The standard MacMichael viscometer was selected because it could be most easily modified for the purposes of this study.

Veegum[a] was chosen as the example of a thixotropic clay, since it could be easily obtained in a standardized form. An attempt was made to determine the manner in which a dispersion of the material changes from a gel to a sol during aging at various temperatures.

Survey of the Literature

Rheology is that branch of physics which deals with the flow of matter. It is based on viscosity, which has been defined as the resistance to the movement of molecules, a movement usually described as flow (1).

The term rheology, in the sense applied here, came into use in 1929, when Bingham and Crawford selected it as distinctive and explanatory for the subjects of elasticity, viscosity and plasticity. An earlier use of the term by Forel, in 1901, seems to have been completely overlooked. The Bingham-Crawford definition has taken precedence, and has become well established (2).

The earliest attempts to measure flow properties of fluids dealt mainly with the principles of capillary viscometry. As early as 3000 B.C., the Sumerians used, as a unit of weight, the quantity of water flowing from a funnel in a unit time. In 1540 B.C., Amenemhet

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[a]Available from R. T. Vanderbilt Co., N.Y., N.Y.

invented a water clock consisting of a conical vessel with a hole in the bottom. Time was measured by the height of water remaining in the vessel (3). The first scientific writings on flow measurement were by Palissy in the 16th century with his thesis being based on the consistency of various soils (4). Leonardo da Vinci investigated the flow of water through orifices and channels at the turn of the 17th century. During the 17th century, Hooke stated that stress is proportional to the strain in elastic solids, and Newton observed that resistance to flow is proportional to the rate of shear in liquids. As his model, Newton used a rotating cylinder in a pool of water, which is the basis of many rotational instruments in use today. It is doubtful if Newton realized how important his concept would be on modern rheology, since he was using his model to investigate the rotation of planets in the solar system. Modern rheologists view Newton's law as an idealized example in which the rate of shear is directly proportional to the shearing stress. However, a great number of pharmaceutical materials generally exhibit non-Newtonian flow, the rate of shear being disproportionate to the shearing stress.

Probably the first scientific experiment in which a capillary tube was used to measure flow was made by Hagen in 1839, followed shortly thereafter by the work of

Poiseuille. Poiseuille studied capillary flow problems in order to better understand the circulation of blood through the capillary vessels in the human body. He discovered the relationship between flow rate and pressure drop for capillary flow known as the Hagen-Poiseuille law (5). Van Wazer et al. state that the studies were made with water, while Haynes states that the studies were on blood (3,6). The discovery of Poiseuille was the foundation of capillary viscometry. Following Poiseuille, Wiederman and, later, Hagenbach deduced a theoretical formula for Poiseuille's discovery based on Newton's definition of viscosity. With the developments in hydrodynamics and advances in the technology of non-Newtonian fluids, capillary viscometry became a reliable method of measuring flow properties of fluids. Until 1890, when Couette devised a new method based on a system of two concentric cylinders, capillary flow was the only widely used technique in viscometry (3).

Bingham, the father of current rheology, studied a diverse group of substances from water to blood. He emphasized the fact that seemingly physically or chemically different substances will mechanically behave similarly when they deform (7). Bingham noted that the Greek philosopher Heraklitus stated that everything flows, and the motto of rheology has become "all things flow (8)."

The Montmorillonite Clays

Damour and Salvetat proposed the name montmorillonite for a mineral from Montmorillon, France, in the year 1847. This mineral was hydrous aluminum silicate, and Ross *et al.* established the montmorillonites as a valid clay-mineral group. The expanding lattice structure of montmorillonite, considered to be an essential characteristic of the mineral, was reported by Hofmann, Endell and Wilm in 1933. The term montmorillonite is used both as a group name for all clay minerals with an expanding lattice, except vermiculate, and as a specific mineral name. The name indicates a high alumina end member of the montmorillonite group with some slight replacement of aluminum by magnesium and substantially no replacement of silicone by aluminum. The empirical formula is given as $(OH)_4Al_4Si_8O_{20}{}^{\circ}xH_2O$ (9).

The montmorillonites display a phenomenon known as plastic viscosity and are thixotropic in nature, in proper concentrations (11). Any substance, as the montmorillonite clays, showing an isothermal reversible change from a higher to a lower viscosity gel is said to be thixotropic (4). The degree of thixotropy of a substance can be determined by finding the area of the hysteresis loop obtained. The hysteresis loop is

prepared from observations of rate of shear and shearing stress as the rate of shear is increased to a predetermined point and then decreased to the original value or lower. If the curves do not coincide, a hysteresis loop is formed which will exhibit the thixotropy of the system. Figure 1 indicates the degree of thixotropy as manifested by the hysteresis loop. Here the loop increases with concentration (12). A two hour rest period has generally been found adequate for a thixotropic substance to return from its sol state to the gel (13).

Martin and van Olpen attempted to explain the phenomenon of thixotropy by postulating that the particles or platelets in the dispersion behave in a fashion somewhat similar to arrangements of playing cards. The "card house" theory proposes that the platelets or particles may associate in three different fashions, which are edge to edge, edge to face and face to face. These three modes of association are regulated by three different net potential curves of interaction, since the edge and face double layers are different, and since the van der Waal's interactions in the three positions of approach are different. The types of association may occur simultaneously, but often one type predominates, depending on the clay and the flocculation conditions. The effect of the three modes of association on the rheologic properties of

suspensions are different. Edge to edge and edge to face association leads to the formation of voluminous three dimensional card-house frameworks, whereas face to face association merely results in thicker plates. Therefore, the first two types of association lead to the creation of gels at comparatively low clay concentrations, whereas face to face association results in a decrease of the number of particles per unit weight of the clay available for the building of a framework, and thus reduces the tendency of the system to gel (14,15). This theory of a three dimensional array of particles has been studied and verified (16).

Hahn, Ree and Eyring introduced a theory of entangled molecules which become disentangled upon application of stress as shown in Figure 2 (17). The container wall is thought to have an organizing effect on the clay particles, and may produce an apparent increase in viscosity in small containers (18).

Factors which also may affect viscosity are the particle size of the dispersed phase and the nature of the ingredients, the arrangement or packing of these particles in the dispersion medium, the volume of dispersion medium in relationship to the dispersed phase, the ease of orientation of the molecules to one another in the system, the polarity and chemical constitution of the

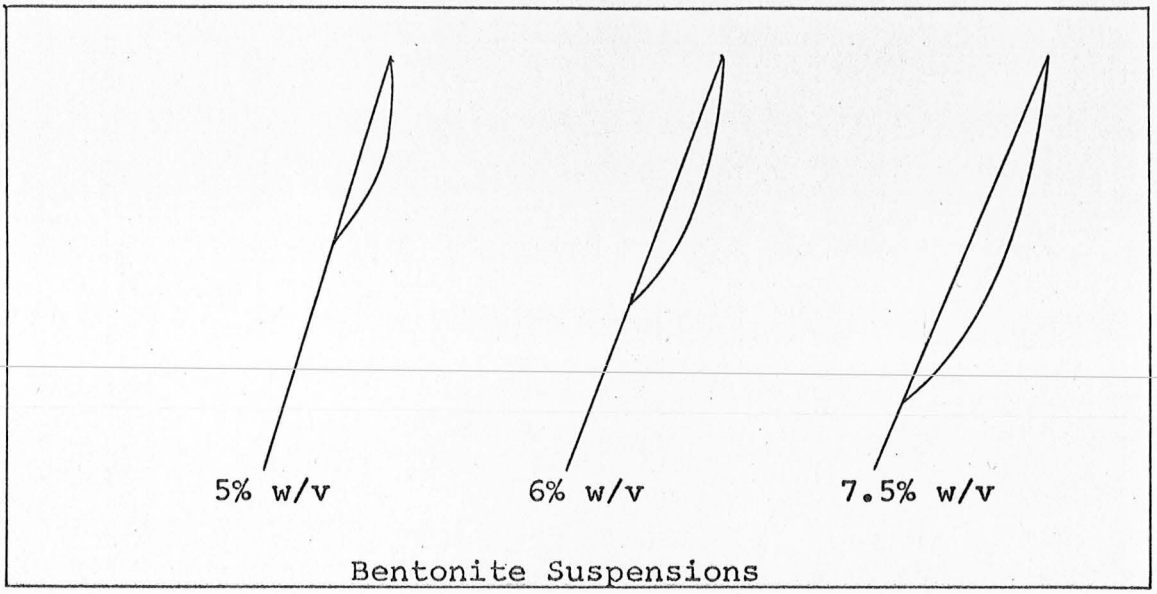

Figure 1. Thixotropy and Concentration (12)

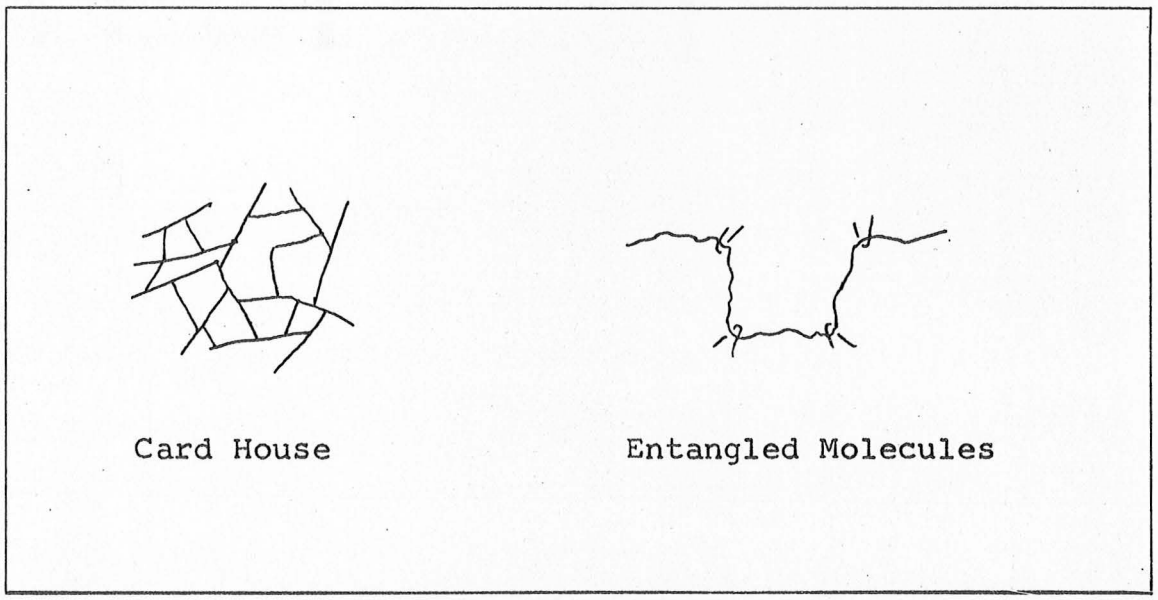

Figure 2. Structures in Thixotropic Materials (14)

ingredients (4,19), and the sterility of the system (20).

Thermal history and previous mechanical treatment affect the rheologic properties of non-Newtonian systems, but the application of heat in the preparation of montmorillonite clay dispersions is said to not affect the final product significantly (18,21,22). Elevation of the temperature of the dispersion during hydration results in a more complete hydration (23). Heat and age permanently increase the viscosity of montmorillonite mixtures in water, although such effects become insignificant in more viscous dispersions (11). Wood and Catacalos have found that the aging of Veegum systems has a log-time log-viscosity relationship (24).

Altering the speed on a high shear mixer and colloid mill apparently has little effect on the thixotropic index, which is a relation of the area of the hysteresis loop. A homogenizer produces a greater yield value, i.e. the amount of applied stress required to produce flow, than does the colloid mill. The colloid mill, in turn, is more effective than the high shear mixer. Accordingly, the homogenizer would appear to be the best method of dispersing solids in a system (23). It is recommended that a clay dispersion be homogenized before use, in order that a smoother dispersion with more complete hydration be obtained.

Flocculation in these clay systems indicates presence of van der Waal's-London interatomic attractive forces. These forces operate between all of the atoms of one particle and all of the atoms of another. Repulsion is due to electrophoresis. Flocculation by electrolytes is not a matter of particle size reduction, but reduction of the range of repulsive forces by compression of the diffuse double layer (15). Certain electrolytes will cause flocculation in the order of activity from monovalents which are mildly active, divalents which are more active, and trivalents which are most active. If an electrolyte is added to a thick slurry, in which the clay has been hydrated and swelled, the consistency of the slurry will be increased, but if the water is first treated with the electrolytes and the clay put in later, the dispersion will be thinner than a mixture of clay and water. Sodium citrate or sodium phosphate decrease the thixotropic state of bentonite suspensions, and thixotropy cannot be induced in three percent w/v bentonite suspensions to which these salts have been added where thixotropy has been shown to not be present originally. Electrolytes generally tend to increase yield value. Cations of chlorides produce greater water separation in three percent and five percent suspensions than do the anions of sodium salts. Aluminum,

magnesium and calcium were found to produce the greatest amount of water separation (11,24). Certain preservatives are said to lower viscosity initially, but produce a slight increase in viscosity upon standing (25). In most instances, the inclusion of alcohol will decrease the viscosity of these systems (11,24). Bismuth salts, such as bismuth subnitrate, are incompatible with Veegum (26).

Veegum, a magnesium aluminum silicate of the montmorillonite clay series, exhibits a pH of about 9 in a four percent suspension. Depending upon the concentration employed, a wide range of physical properties may be observed. In concentrations of less than one percent, in water, this clay can be used as an emulsion stabilizer. When the strength of the suspension is increased into the range between one and two percent, thin colloidal dispersions are formed. White, thixotropic dispersions are formed at a concentration of three percent, the degree of thixotropy being inversely dependent upon the size of the container in which the material is stored. White, thick, opaque sols are formed at concentrations between four and five percent, and a thick gel is formed when a ten percent aqueous suspension of Veegum is prepared (22).

The general pH range of the montmorillonite clays is 8.5 to 9.5 with the pH of the dispersion decreasing as the water ratio increases. The clays will operate within

a range of 6 to 11, but are most effective, viscosity-wise, between pH 9 and 11. Viscosity decreases above and below this range. The reaction resulting in basicity is due to hydrolysis as may be shown with sodium silicate:

$$Na_2SiO_3 + 2HOH \rightleftharpoons H_2SiO_3 + 2NaOH \quad (11,12).$$

Types of Rheologic Flow

This discussion is limited to those flow patterns obtained when using rotational viscometers. Figure 3 summarizes, graphically, the types of flow patterns generally observed when using rotational viscometers in the investigation of rheologic behavior of various materials. The abscissa represents the amount of applied stress, while the ordinate represents the rate of shear.

In the case of Newtonian substances, the rate of shear is directly proportional to the amount of stress applied. Therefore, a single point can be used to determine the curve, as it is always a linear graph with the second point at the origin. Newtonians exhibit isothermal flow and generally are pure liquids or true solutions.

Other types of flow are classed together as non-Newtonian under the subtitles of plastic, pseudoplastic and dilatant. The factors involved in causing these differences from Newtonian flow have been ascribed to the

particle size of the dispersed phase and nature of the ingredient, the arrangement or packing of these particles in the dispersion medium, the volume of dispersion medium in relation to the dispersed phase, and the ease of orientation of log-chain molecules to one another and to other molecules in the system. Figure 4 shows how the systems might appear if the particles were large enough to view, and demonstrates what occurs when shear is applied to the system.

Materials exhibiting plastic flow are known as Bingham bodies in honor of Bingham, the first investigator to study plastic substances in a systematic manner. The curve in a graph for plastic flow does not pass through the origin, but intersects the shearing stress axis at the point designated as the yield value. A plastic material will not flow until a shearing stress corresponding to the yield value is exceeded. Plastics, or those substances which begin to flow at the smallest shearing stress are defined as liquids. The curve for a plastic material in nonlinear at low shear rates as observed in the graph of Figure 3. This characteristic is attributed to plug flow, caused by the material moving as a solid plug near the walls of the cup at low shear rates. As the rate of shear is increased in a properly designed instrument, the

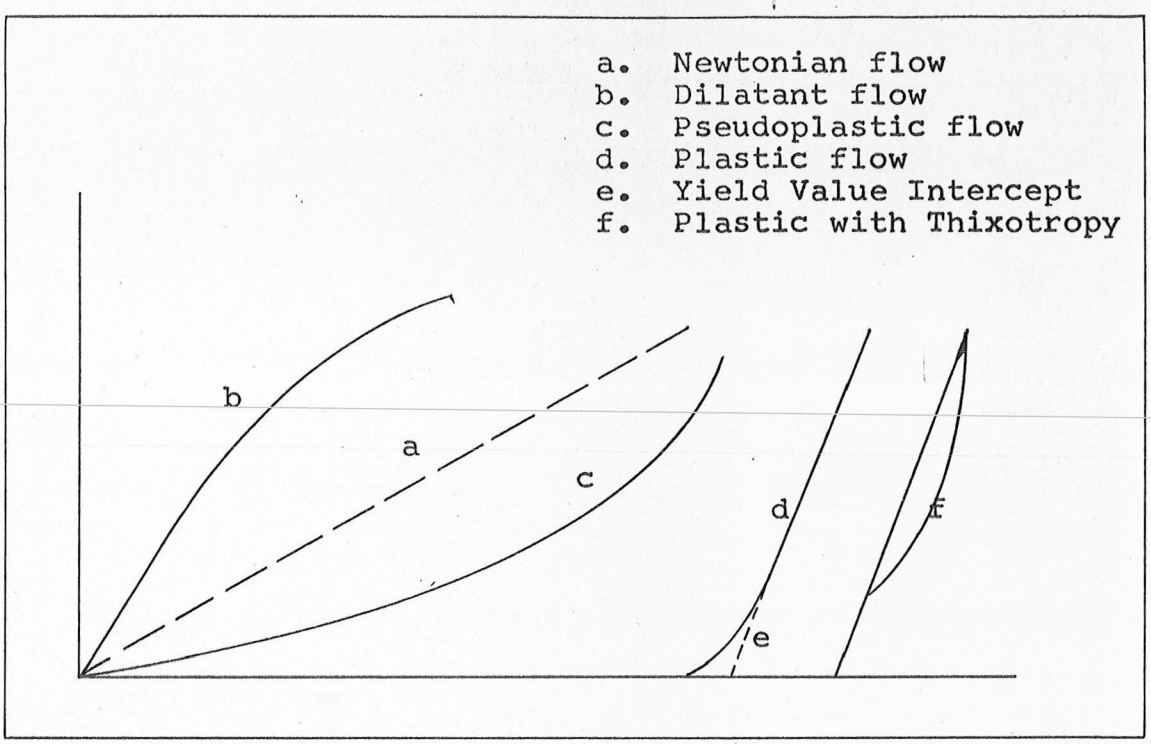

Figure 3. Flow Patterns with Rotational Viscometers (4).

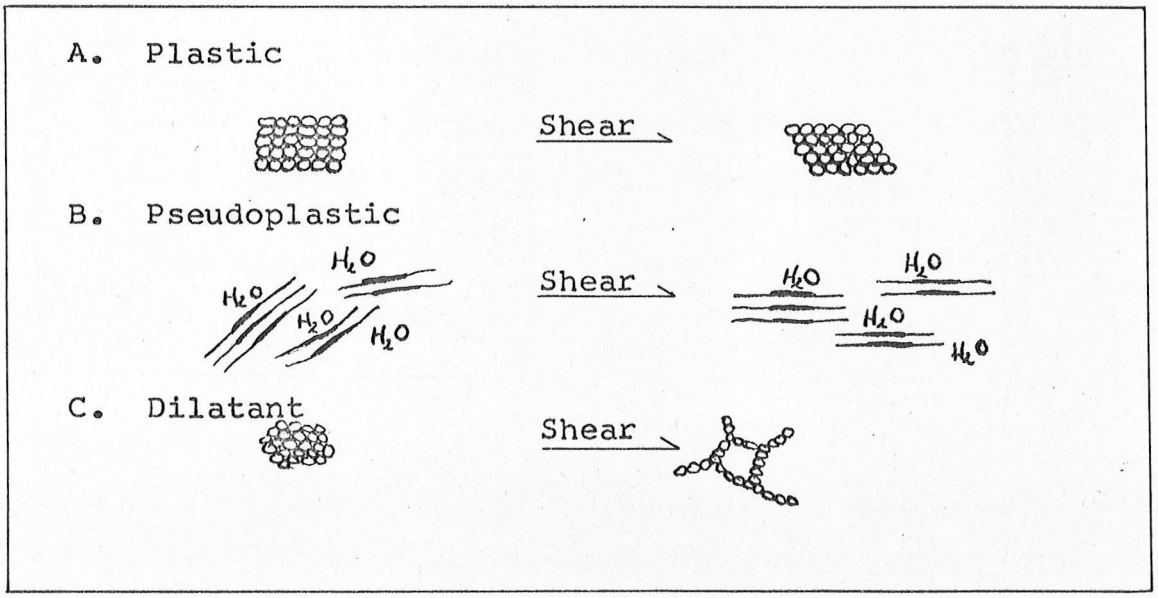

Figure 4. Types of Flow (14).

substance begins to flow as lamellar layers throughout its mass, and the curve relating shearing stress to the rate of shear becomes linear. Complex plastics are frequently found to manifest the additional property known as thixotropy. This phenomenon is usually referred to as an isothermal gel-sol-gel transformation, characterized by the breakdown of structure with agitation, and followed by the reformation of a rigid structure, when the material is allowed to stand undisturbed for some time. Examples of this property are the montmorillonite clay suspensions and petrolatum (4, 14). Hahn states that the characteristics of thixotropy are the result of a structural change brought about by applying mechanical disturbance to a system, and when that mechanical disturbance is removed, the system reverts to its original structure. The flow curve of the system will show a hysteresis loop (16). Hahn uses his theory of entangled molecules which become disentangled upon the application of stress. Other theories involved here are the card house theory of Michaels and the block house theory of Eyring (14). The block house arrangement is applicable to highly concentrated suspensions, the block house structure being continuous throughout the mass.

The curve for pseudoplastic materials begins at the origin or at least approaches it at low shear rates. Since no part of the curve is linear, the viscosity of a

pseudoplastic material cannot be expressed by a single value. The viscosity decreases with increasing shear rates. An apparent viscosity may be obtained at any rate of shear on the curve, but the most satisfactory representation is a graphical plot of the entire curve. The up-and down-curves of a pure pseudoplastic material coincide. It is thought that the curves result from a shearing action on the long chain molecules of materials such as linear molecules. As the shearing stress is increased, the molecules begin to align with the long axes in the direction of flow. This orientation reduces the internal resistance of the material and allows a greater rate of shear at each successive shearing stress. Since there is no thixotropic breakdown, but only a molecular alignment, there is no time lag in the return of the molecules to the disordered state. Hence, the downcurve coincides with the upcurve. Examples of pseudoplastics are tragacanth and methylcellulose dispersions.

Dilatant materials are substances whose resistance to flow increases as the shear increases. Dilatancy in a system depends on close packing of the dispersed particles and deflocculation. Particle shape also appears to be important, since it has been observed that spherical solids reach a maximum dilatancy at a higher solid concentration than those particles having irregular or

cubic shapes. The size of the particles may also be involved. The creation of dilatancy in a system may be ascribed to the settling of particles in such a way that at rest they are close to one another, but not linked through any attractive forces. In this state, a minimum volume of liquid surrounds each particle and acts essentially as a lubricant when the dispersion is poured. However, when more stress or agitation is transmitted to the system, the particle become rearranged, with larger voids among them. These larger voids then pull in the liquid, depleting the lubricant from the many surfaces of other particles. The net result is that the particles pile up on one another, producing a system resembling a solid. Pastes, pigments used in the printing industry, concentrated suspensions of titanium dioxide and "Silly Putty" are examples of dilatant systems (4,14).

Instrumentation

Many instruments have been devised for rheologic study with rotational instruments being found best adapted for rheologic studies. They are basically of two types, the Searle and Couette. In the Searle type, the cup is stationary and the inner part rotates. In the Couette type, the inner part is stationary and the cup rotates.

The Stormer viscometer and its modifications and the Brookfield viscometer and its modifications are Searle type. In the case of the Stormer, the time for the bob to rotate one hundred times is measured, giving an average number of revolutions per minute or the rate from zero through one hundred revolutions. The Brookfield measurement is based upon a torsion transmitted to a spring inside the instrument. Readings from the calibrated dial will yield the viscosity of the sample when used in conjunction with the "Factor Finder Chart" supplied with Brookfield instruments.

The MacMichael viscometer is an example of the Couette type of instrument and the readings are based upon the torque transmitted through a torsion wire, which may be changed for different viscosity materials. Viscosity is determined using a constant for the wire after testing with viscosity standards. The torsion wire instruments give final readings after the sample is tested in the instrument for a specified length of time. However, the occurences before the readings are taken from time zero to the end of the reading period are not observable in these instruments as supplied from the manufacturer. Recording instruments are available, but in most cases, there is some strain placed on the instrument which makes it less sensitive than normal due to an extra drag or

torque. Examples are the Feranti-Shirley cone and plate viscometer, the Hercules High-Shear viscometer, the Brabender Visco-corder, the Corn Industries viscometer, and the Visco-Amylo-Graph (29).

A viscometer with a glass bob designed by Zimm and Crothers has been modified by Quadrat and Munk. Quadrat and Munk modified it to be automatic recording by means of a photoelectric device (30,31).

C H A P T E R I I

EXPERIMENTAL I

Preparation and Standardization of the Modified MacMichael Viscometer

The Fisher Improved MacMichael viscometer[a], as supplied by the manufacturer, is a rotating cup or Couette type of instrument. A calibrated torsion wire is inserted through a spindle with the bottom of the wire connected to the spindle and the free end connected to the viscometer pylon by slipping the triangular hanger behind the supporting bolts. A bob is connected to the spindle by means of a bayonet clip at its base. The sample cup is filled, and the amount of drag produced upon the bob by the sample in the rotating cup is measured in degrees MacMichael on the spindle dial. The speed of the cup rotation is controlled by a graduated knob on the right side of the viscometer base, the rate being determined by counting the number of revolutions in a given time. Degrees MacMichael may be converted to absolute units by standardizing the instrument against viscosity standards or by using wires of known torque constants. The wire and spindle must be removed each time the sample cup is to be removed for filling or cleaning. A dash pot, attached to the spindle and pylon, may be filled with glycerin or light mineral oil to damp large oscillations of the spindle assembly during testing.

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[a]Obtained from the Fisher Scientific Company, Pittsburgh, Penna.

Modifications

The pylon of a MacMichael viscometer was cut horizontally just below the dash pot mount. The arm, coarse adjustment mechanism and body tube rack of a microscope were bolted to the sections of the pylon with the adjusting mechanism and body tube rack fixed to the top section of the pylon, and the lower end of the arm bolted to the viscometer base. This arrangement provided a means of removing the test probe without removing the torsion wire, while at the same time affecting minimal destruction of the sample. A third hole was threaded into the torsion wire mount for a bolt to prevent dislodging of the spindle assembly during unusual stress and insertion of the test probe into the sample. An event marker was mounted on the base of the viscometer, as shown in Figure 5, and wired in order that each revolution of the sample cup would be noted on the recorder.

An enclosure, for a photoelectric sensing system, consisting of a base and removeable cover, was fabricated from 1/8 inch plastic stock, as shown in Figure 6. After preparation of these sections, the inside of the entire assembly was painted flat black and covered with black velvet to minimize leakage of light. The enclosure was constructed in such a manner that the top and sides could be removed easily for necessary adjustment of the system. A 1½ inch slit was cut into the top center of the cover so the box could be removed to adjust the diaphragm and avoid friction between the cover and torsion wire. The velvet

protruded into this slit in such a manner that it precluded the entry of external light. The base was mounted on a piece of plastic that had been previously prepared to fit into the dash pot mount. This base support had been drilled with a large enough hole to allow free movement of the shaft connected to the torsion wire and to provide for the inclusion of a set of bearings, if desired. The slit lamp light source was bolted into place on the back of the box, and the photoelectric cell[a] was glued into place below and in line with the light source.

The diaphragm, as shown in Figure 7, was prepared by drawing a circle with a crescent inside it, painting the crescent black with ink, and taking a full scale photograph of this. A photographic negative of suitable high contrast was selected and cut to give the diaphragm. The tabs were left to provide easier adjustment of the diaphragm when positioning the system. The largest opening of the diaphragm's crescent was just large enough to give the full exposure of the slit lamp onto the photoelectric cell. The negative was placed between two discs of 1/8 inch plastic, slipped onto a four inch length of 1/8 inch diameter brass rod, and held in place on the rod by collars above and below the discs to prevent slippage. A drill bit chuck[b] was

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[a]Obtained from Clairex Corporation, New York 1, N.Y. Item number CL5M5L.

[b]Obtained from X-Acto Inc./X-Acto Precision Tools, Inc., Long Island City, N.Y. Item--Chuck Adapter number 22A.

attached to the upper end of the rod for attachment to the torsion wires, while the base of the rod was threaded for attachment to a pin holder.

A pin holder bob was turned from a sheet of 5/16 inch sheet plastic to a disc of two inch diameter, a nut being mounted in the center to fit the threaded rod. Holes of 1/32 inch diameter were drilled into the disc, as shown in Figure 8, with one set at a radius of ½ inch and one set at a radius of 5/8 inch from the center of the disc. Holes were drilled and threaded from the sides to each hole for set screws to hold the probing pins in place. The pins[a] were 2-7/8 inches long, and were placed through one set of holes, whereupon the set screws were tightened. The brass rod holding the photoelectric diaphragm was placed through the base of the box and its mount, inserted through a plastic disc to give more weight to the pins, and screwed firmly into the pin holder, as shown in Figure 5. As prepared, the pins penetrated to a depth of 3/8 inch into a sample in a two ounce ointment jar filled to the neck.

A sample holder was prepared, as illustrated in Figure 9, of 3/8 inch sheet plastic. This fitted over the rim of the sample cup of the MacMichael viscometer, and would hold a two ounce ointment jar. This was accomplished by cutting the center out of an ointment jar lid, and mounting this in the center of the sheet plastic with a set of two bolts

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[a]Obtained from The Boye Needle Company, San Francisco, Calif. Item number 750.

and glue.

The power to the light source, photoelectric cell and event marker was supplied by a Heathkit regulated power supply. The ammeter adjustment of the power supply was set for a maximum value of 20 milliamperes at the greatest opening of the diaphragm above the photoelectric cell. Power to the viscometer motor was regulated by a Powerstat with the speed control knob of the viscometer set at its maximum. The Powerstat was selected because its dial could be read and adjusted more easily than the control built into the viscometer. The temperature bath was not used with this arrangement, since the voltage to it was not constant during testing, and the samples were not on the instrument long enough for appreciable temperature change.

Uncalibrated torsion wires were cut to 5½ inches for this instrument. Their triangular anchor was placed into the regular fitting on the pylon, and the third bolt was placed in position. The bottom of the wire was clamped firmly in the chuck.

The deflection of the recorder needle from zero to 100 gives the relative rotation of the diaphragm across the photoelectric cell, and is the value, given as Torque Units, in this study, replacing the degrees MacMichael as the unit of measure.

The sensitivity or magnitude of response of the photoelectric sensing system could be adjusted by appropriate manipulation of the potentiometers within the electronic

control assembly[a]. During this study, settings were initially established and maintained so as to provide maximum response of the recorder during measurement.

Figures 10 through 12 show the over-all arrangement of the apparatus.

Mode of Operation

The instrument was first leveled, and the electrical circuits were checked for proper arrangement and good connections. The power supply was found to operate best if it was allowed to warm-up for a period of at least two minutes before use. Electrical power to the instrument was turned on and off with the controls of the power supply, the electronic control assembly, the recorder drive, the viscometer motor, and the on-off switch of the Powerstat.

The proper pin setting radius and the torsion wire were selected if the approximate viscosity of the sample under test was known. When the viscosity was not known, the wire of greatest diameter was tried, and progressively thinner wires were chosen until the proper wire was found. It was essential that the chuck holding the torsion wire be tight enough that it would not slip while in use.

At the beginning of each day of testing, the photoelectric diaphragm was checked to ascertain that the plastic discs were in place and clean, that the narrowest

---

[a]Designed by Mr. Howell I. Runion, present address: University of Glasgow, Glasgow, Scotland.

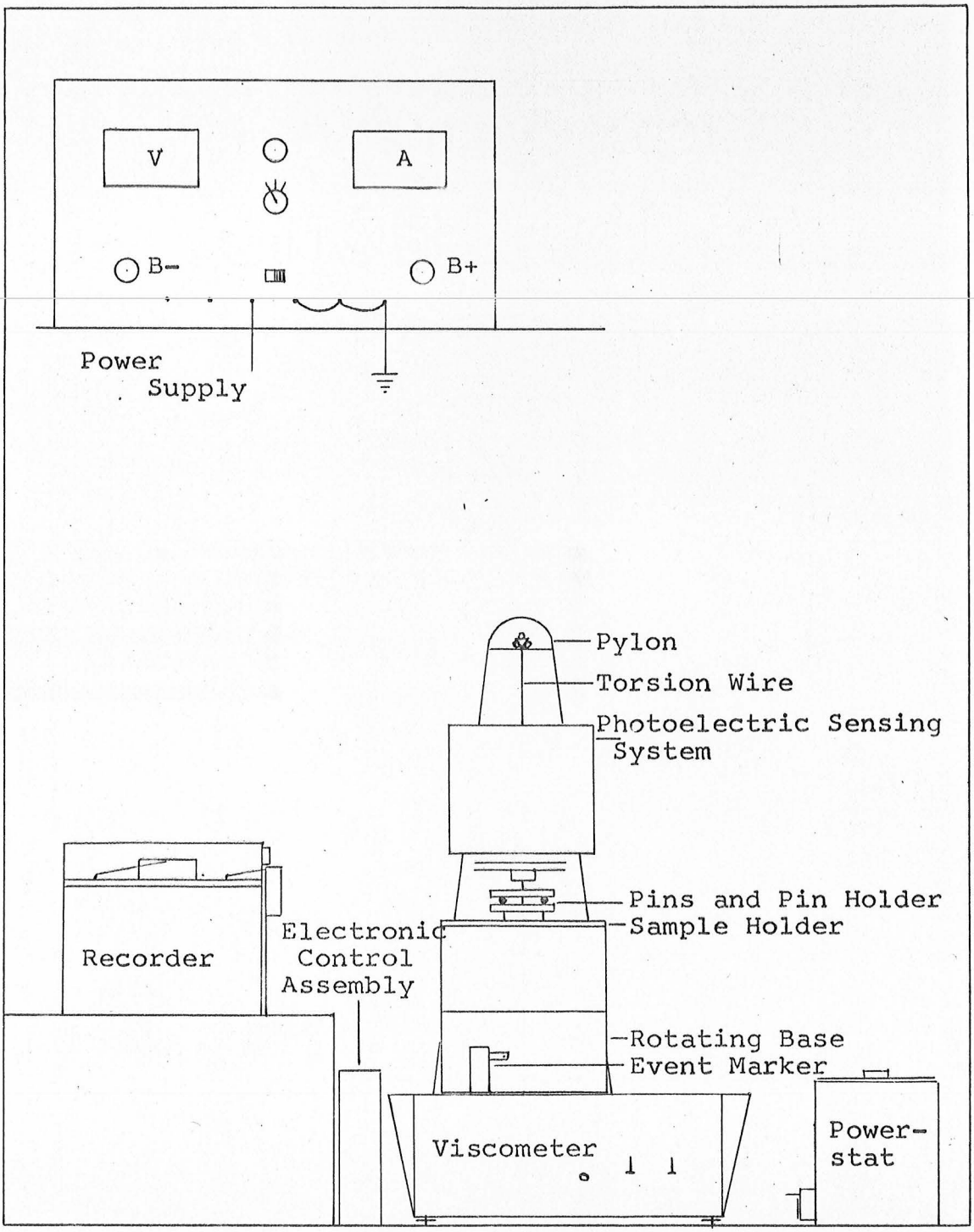

Figure 5. Physical Arrangement of Equipment

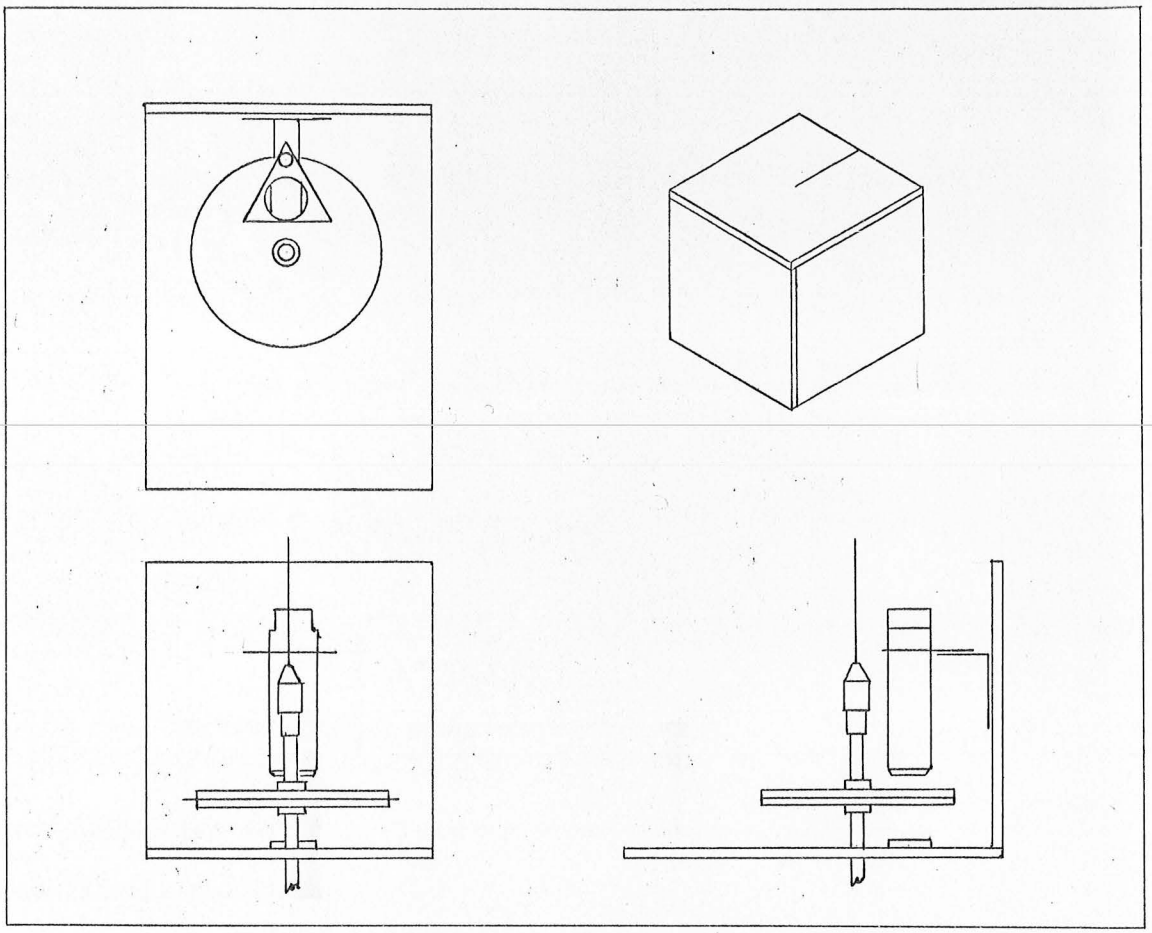

Figure 6. Photoelectric Sensing System

Scale: 1 inch = 2 inches

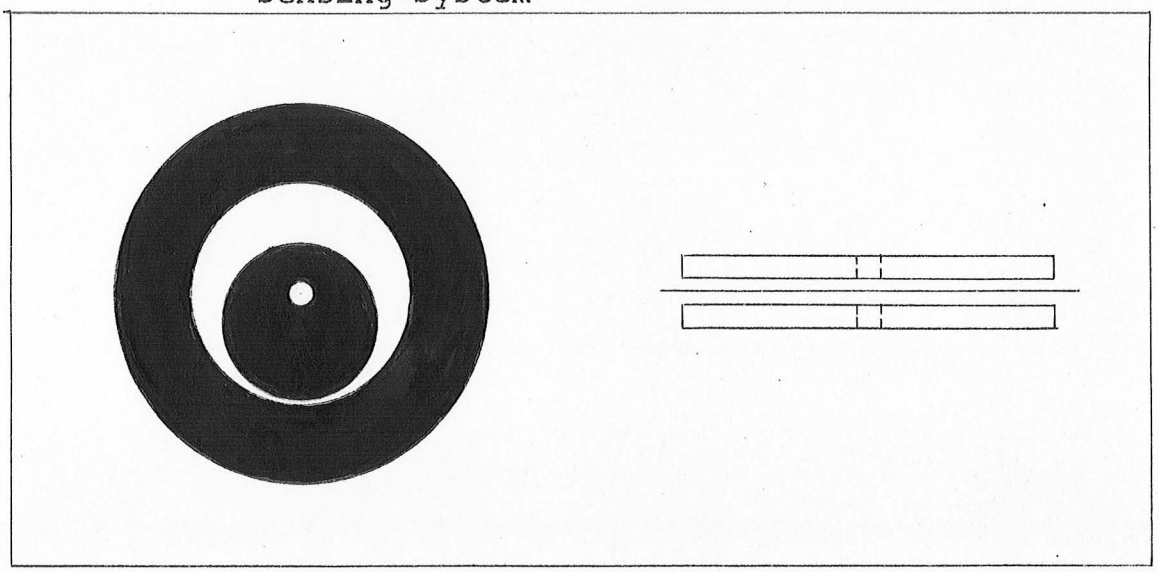

Figure 7. Photoelectric Diaphragm

Full Scale

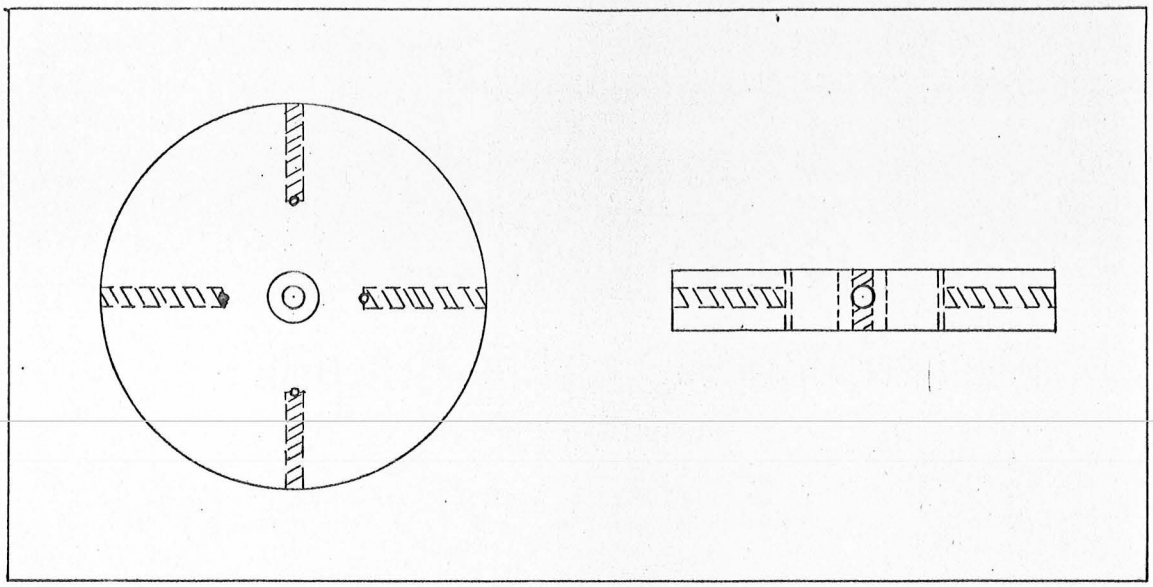

Figure 8. Pin Holder Full Scale

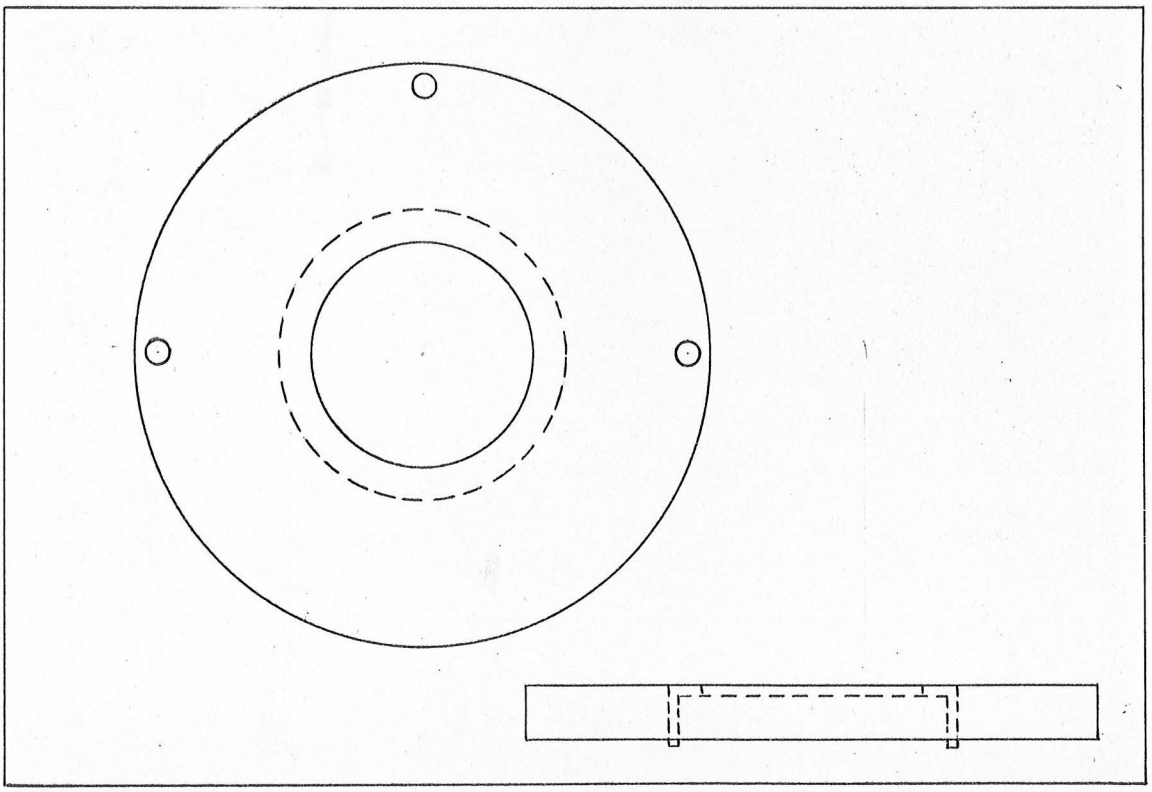

Figure 9. Sample Holder Scale: ¾ inch = 1 inch

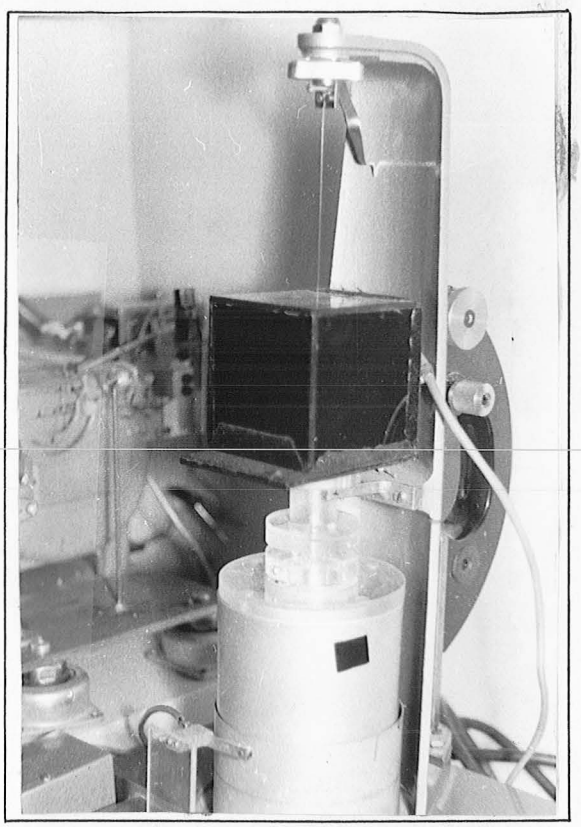

Figure 10. Viscometer Pylon Modifications.

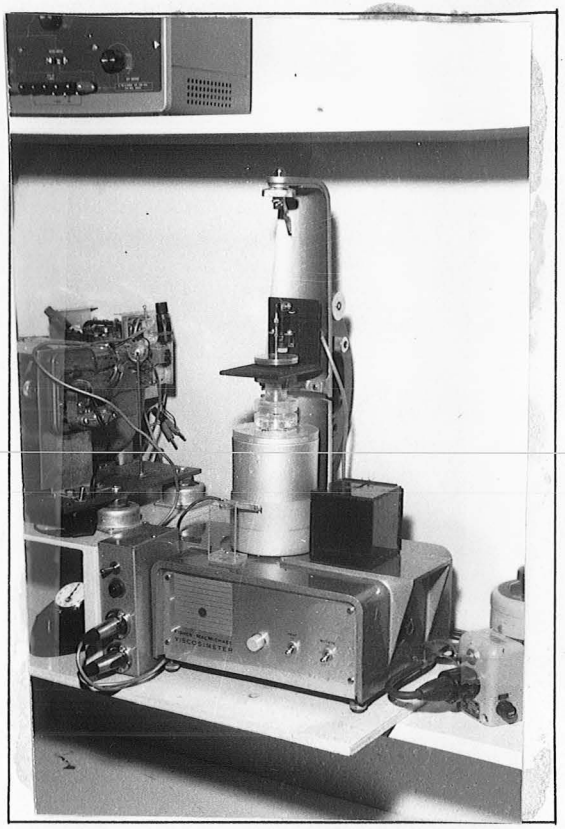

Figure 11. Frontal View of the Viscometer.

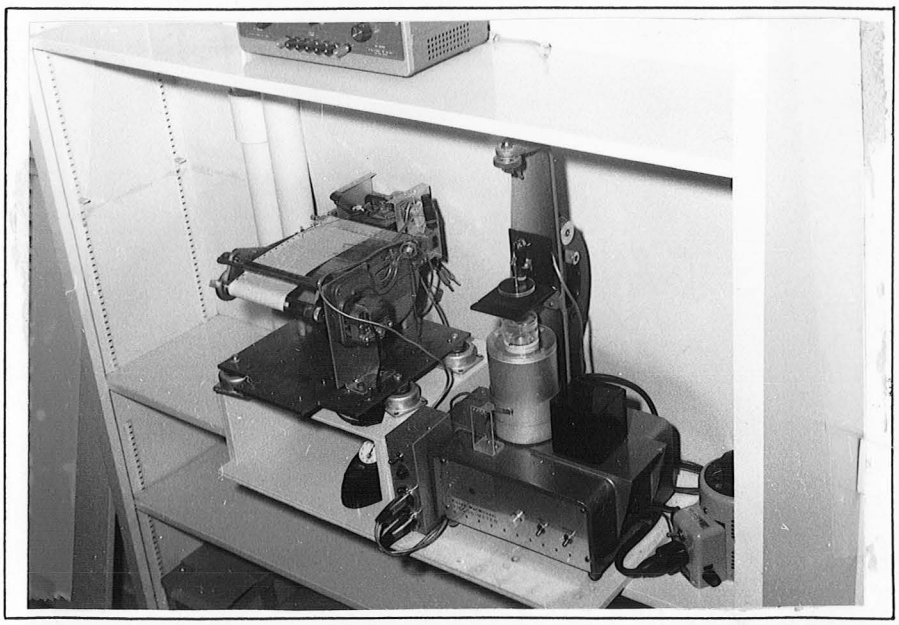

Figure 12. Viscometer from Top-front View.

part of the diaphragm was over the photoelectric cell when at rest, and that the maximum milliampere reading of 20 would be observed at maximum exposure.

Raising and lowering of the top section of the pylon holding the torsion wire and photoelectric system was accomplished by means of the microscope coarse adjustment knob. The sample jar containing the material to be tested was screwed firmly into the sample holder, and positioned into the MacMichael sample cup, aligning the thermometer holes.

If consistent results were to be obtained, insertion of the pins to the same depth for each test was necessary. Greater or lesser pin depths would have resulted in differing degrees of stress upon the pins and unmatched values in samples of the same material. Pin depth into the sample was noted during insertion of the pins into the sample. The pins were wiped clean between each change of rate of shear to prevent the build up of material on the pins.

The samples were tested for predetermined lengths of time in accordance with a selected experimental design, the rate of shear being adjusted by the Powerstat.

Torque units were arbitrarily taken to be the value obtained from the recorder paper on a scale of from zero to the maximum deflection of the recorder needle having a value of 100.

Standardization

The instrument was standardized against prepared aqueous glycerine solutions, the viscosities of which had been determined by using the Mohr-Westphal balance in conjunction with tables of "The Handbook of Chemistry and Physics (32,33)," and Brookfield viscosity standards[a]. The standardization was performed on each torsion wire prepared for the study. Each wire was tested with the viscosity standards at a temperature of 25° C. at several rates of shear. All materials were tested in two ounce ointment jars in order to have greater uniformity, since the size of the sample cup is known to affect the viscosity measurements. The Stormer viscometer samples were held in place by means of a piece of rubber tubing around the jar when in position in the sample cup of the instrument. The Brookfield LVT viscometer with its number 4 spindle was mounted on a Helipath[b] stand for support only. The number 4 spindle was selected as the test probe because it was best suited in terms of size for the sample container used.

EXPERIMENTAL II

Testing the Rheologic Properties of a Veegum Dispersion with the Modified MacMichael

A five percent Veegum dispersion was prepared for rheologic testing with the Modified MacMichael, Stormer and

---

[a]Obtained from Brookfield Engineering Laboratories, Inc., Stoughton, Mass.

[b]Obtained from the Brookfield Engineering Corporation, Stoughton, Mass.

Brookfield LVT viscometers.

The dispersion was prepared in a Day-Solver[a] by slowly adding 900 grams of dry Veegum to 16,000 ml. of boiling distilled water. The clay was dispersed using the lowest speed of the Day-Solver for 15 minutes after the last of the clay had been added. After hydration of the clay, 32.4 grams (0.18% w/v) of propylparaben and 3.6 grams (0.02% w/v) of methylparaben were dissolved in boiling water and added to the clay dispersion in the Day-Solver for another 15 minutes mixing at the lowest speed of 1000 revolutions per minute. The dispersion was then transferred to a carboy calibrated to 18,000 ml. and brought to a final volume of 18,000 ml. While still hot, the clay dispersion was passed through a Tri-Homo Disperser Homogenizer[b] twice, the first pass at a setting of seven and the second pass at a setting of four.

In order that the amount of water separation might be observed a 100 ml. cylindrical graduate was filled to volume, stoppered with a wax coated cork, sealed with molten wax, and stored undisturbed. A set of 20 10 ml. test tubes was filled and stoppered with corks covered with plastic sheeting. These were to be centrifuged to determine any settling of the clay upon standing. The test tubes were divided into three equal groups and stored with the samples to be tested

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[a]Obtained from the J.H. Day Company, Inc., Cincinnati 12, Ohio. Model 100.

[b]Obtained from the Tri-Homo Corporation, Salem, Mass. Size 2, Model LA, Sanitary Type.

for rheologic properties. Two of the test tubes were centrifuged at 2,000 revolutions per minute for 20 minutes on the day of preparation, and two from each storage temperature were studied under the same conditions on each day of rheologic testing. The remainder of the Veegum dispersion was poured into two ounce ointment jars and capped immediately. A set of 18 samples was set aside for testing on the day of preparation, as soon as they had cooled to room temperature. The day of preparation of the samples was considered to be Day 1 of the study. The remaining packaged samples were divided into three equal groups with one set stored at room temperature, one set stored at 37° C. and another set stored at 42° C. for aging. Room temperature was the temperature of the laboratory in which the samples were stored and tested. The temperature of the room was noted to vary from 19° C. and 28° C. during the aging period.

Since fissuring and cracking of samples had been observed in preliminary testing, it was decided to measure the moisture content of dry Veegum and samples which had been used for rheologic studies. This test was accomplished with a Cenco moisture balance.

Rheologic testing with the viscometers was done in the manner previously described to obtain the hysteresis loop. This was carried out at a temperature of $\pm$ 1° of 25° C. At least three different weights were used with the Stormer

viscometer, all eight speeds for time periods of one minute each were used with the Brookfield LVT, viscometer and Powerstat settings of 50, 60, 70, 80, 90 and 100 for time periods of one minute each were used with the modified MacMichael viscometer. The pins of the modified MacMichael viscometer were set at the 5/8 inch radius for all testing, and raised out of the sample to be cleaned as each Powerstat setting was made. This was done to allow the pins to return to their original position and assure that they were not being held in the sample at a deflected position thereby leading to spurious results.

The values used to prepare the rheograms of the modified MacMichael studies are averages taken from the recorder paper after a maximum value has been reached and the viscosity has begun to decrease.

C H A P T E R I I I

RESULTS

Experimental I
Viscometer Standardization

Aqueous solutions of glycerin having specific gravities of 1.1547, 1.1850 and 1.2048, as determined with the Mohr-Westphal balance, were prepared as viscosity standards. At 25° C. they are 60 to 61 percent w/v with a viscosity of 9 cp., 71 to 72 percent w/v with a viscosity of 18.4 cp. and 79 percent w/v with a viscosity of 50.6 cp. respectively as determined using the values of "The Handbook of Chemistry and Physics." These were used in conjunction with the Brookfield viscosity standards having viscosities of 1,005 cp., 12,250 cp., 30,500 cp. and 59,000 cp. at 25° C.

Table 1. Standardization of the Stormer Viscometer[a]

Wt. (Gm.)	Water	9 cp.	18.4 cp.	50.6 cp.	1,005 cp.	12,250 cp.
50	882.4	379.7	176.4			
75	1111.1	508.4	256.4	116.3		
100	1304.3	638.2	326.0	152.2		
125	1578.9	750.0	416.6	200.0		
150		810.8	468.7	225.5		
200		967.7	612.2	306.1	48.7	
250		1304.3	731.7	375.0	60.0	
300		1428.5	857.1	441.1	70.5	
400			1071.4	566.0	101.6	
500			1250.0	681.8	120.0	9.8
525			1304.3	714.2		

[a]Values in revolutions per minute.

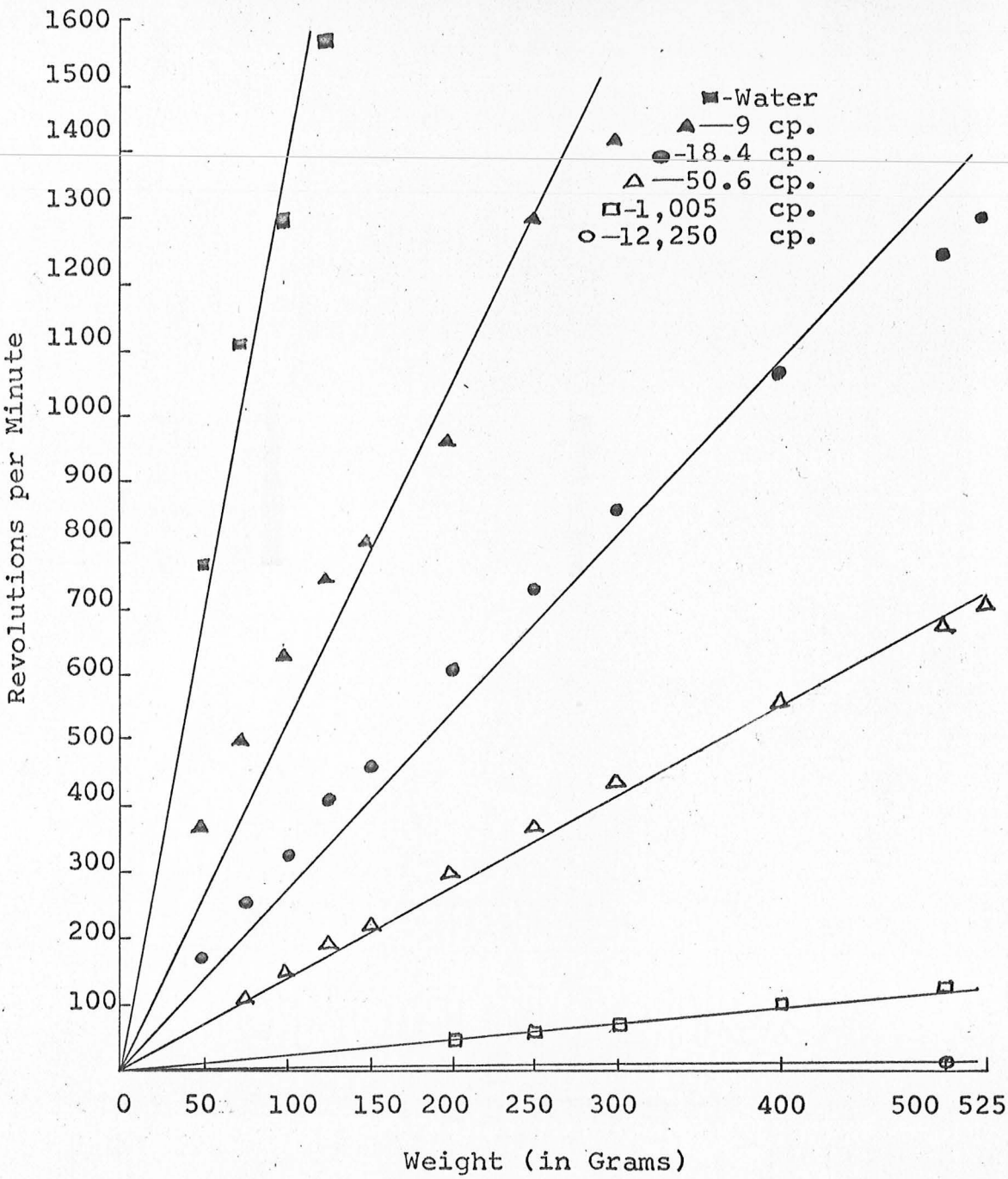

Figure 13. Standardization Curves of the Stormer Viscometer at 25° C.

Table 2. Standardization of the Brookfield LVT Viscometer[a]

RPM	18.4 cp.	50.6 cp.	1,005 cp.	12,250 cp.	30,500 cp.	59,000 cp.
0.3				0.6	1.5	3.4
0.6				1.3	3.0	6.8
1.5			0.2	3.0	7.6	17.0
3.0			0.5	6.0	15.2	34.0
6.0		0.2	1.0	12.1	30.4	68.4
12.0		0.4	2.0	24.2	61.2	
30.0	0.5	1.0	5.0	61.0		
60.0	0.6	1.7	10.0			

[a]Values in Brookfield Dial Units using the Number 4 Spindle.

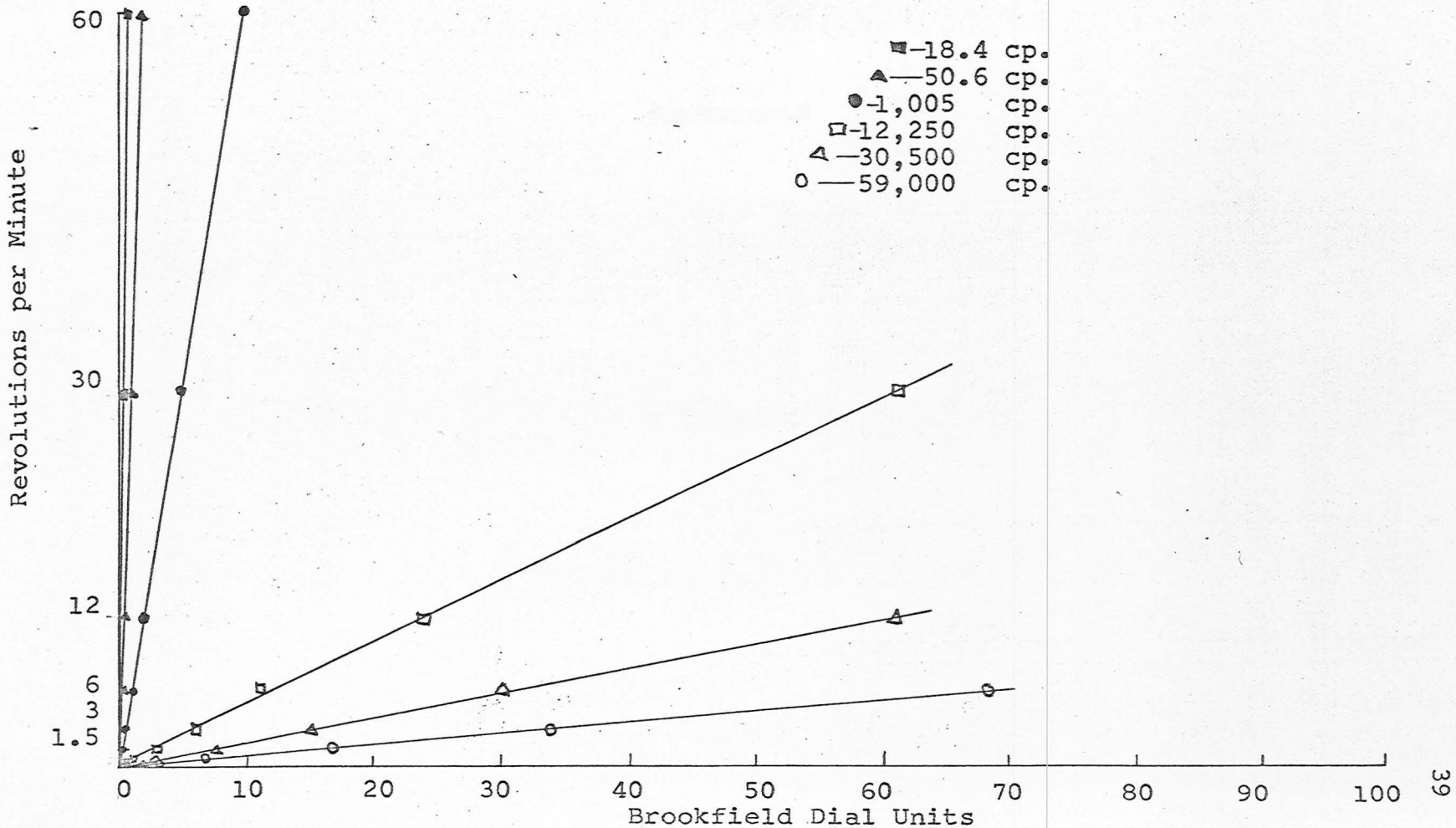

Figure 14. Standardization Curves of the Brookfield LVT Viscometer (Using the Number 4 Spindle) at 25° C.

Table 3. Standardization of the Modified MacMichael Viscometer[a]

1,005 cp.				12,250 cp.				30,500 cp.				59,000 cp.			
Wire #30		Wire #28		Wire #28		Wire #24		Wire #24		Wire #22		Wire #24		Wire #22	
RPM	TU[b]	RPM	TU	RPM	TU	RPM	TU	RPM	TU	RPM	TU	RPM	TU	RPM	TU
12	12			11	34	14	1	14	12			15	51	15	7
24	25	24	1	24	77	24	2	24	27			24	89	25	22
30	32	32	2			33	3	34	44	32	8			34	36
40	39	40	3			43	4	42	58	41	12			40	46
47	52	47	4			46	6	46	69	48	13			48	57

Note: There were no observable readings using the standards of less than 1,005 cp. with the torsion wires of this study.

[a]Values in Torque Units using a Pin Setting of 5/8 inch radius, 3/8 immersion depth.

[b]TU= Torque Units.

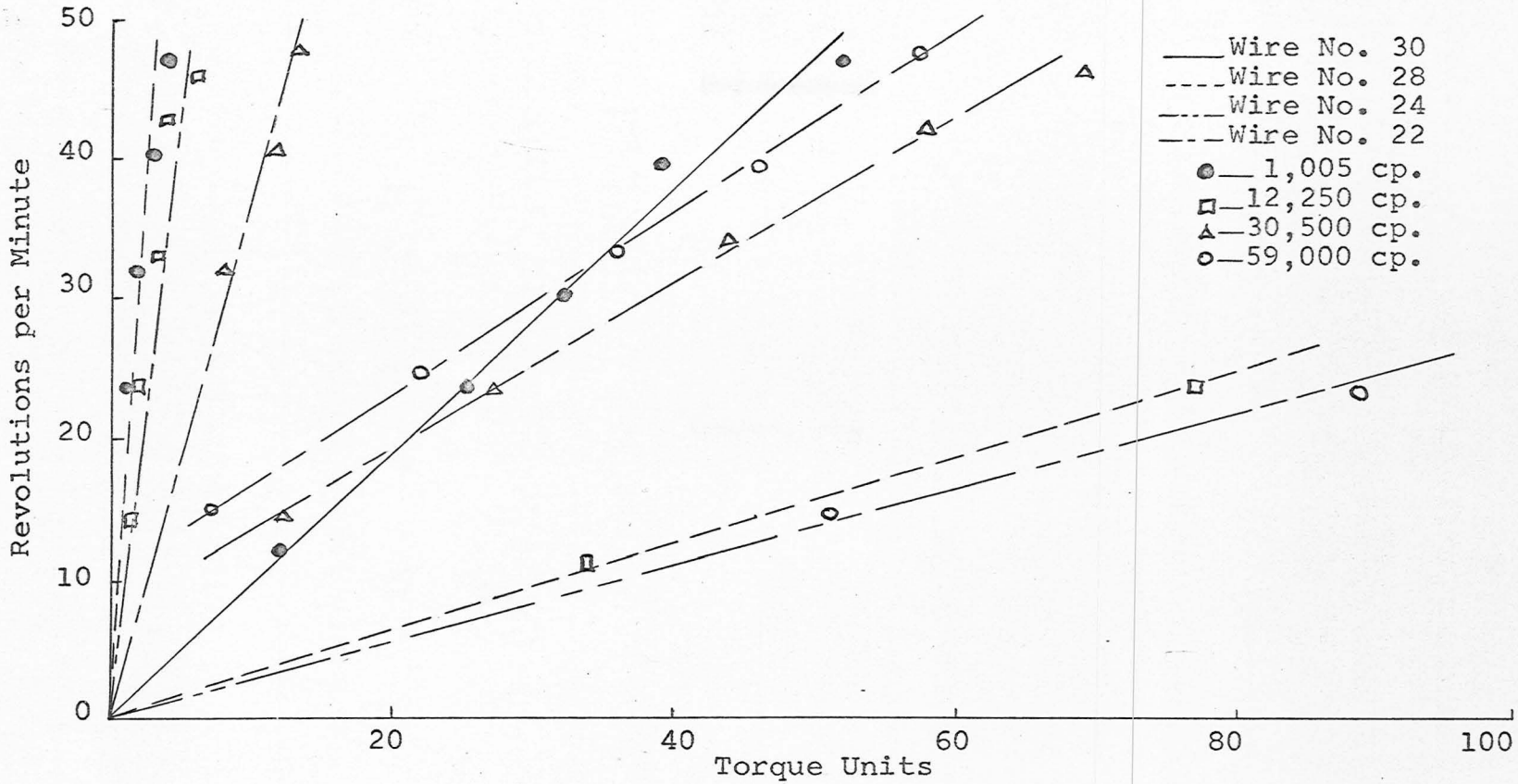

Figure 15. Standardication Curves of the Modified MacMichael Viscometer at 25° C.

Experimental II
Study of an Aging Veegum Dispersion

Centrifugation of the test tube samples throughout the time of the study exhibited no separation of water from the dispersion, as had been noted in a previous study in which 0.2 percent sorbic acid had been used as the preservative. The sealed cylindrical graduate containing the dispersion yielded less than 0.5 ml. of supernatant water on the sample at the end of 97 days.

A moisture balance examination of the dry Veegum used to prepare the dispersion had an average of 7.5 percent moisture. The results of moisture balance studies of the aged Veegum dispersion, stored at room temperature, are reported in Table 4.

Table 4

Percent Moisture Content in Aging 5 Percent Veegum Dispersion Stored at Room Temperature

Day 1	Day 97	Day 311
95.4	95.2	95.1

A set of six samples which had been stored at 42°C. for 99 days had an average moisture content of 94.1 percent. Even though all lids had been tightened securely on the day of preparation, some appeared to be loose in this set at the time of testing, possibly due to expansion during storage at the elevated temperature.

Table 5. Stormer Viscometer Results[a]

Temperature:									
Wt. (Gm.)	Day:	Room				37° C.		42° C.	
b	1	2	4	7	37	2	4	2	4
75	21.5	19.2				3.1			
100	79.0	62.8	39.3			45.5	10.0	13.5	
125	219.0		132.1	82.7		92.4	45.7	61.7	
150	350.0	324.3	235.4	189.1		293.0	97.3	123.5	31.1
200			550.0	550.7			274.8		147.2
250				824.0					
300					86.2				
400					385.8				
500					1171.1				1353.4
525					1316.2				
500					1240.0				
400					995.8				
300					596.3				
200				657.4					427.3
150			381.4	437.3			180.1		230.7
125	325.0	288.5	318.1	338.1		248.0	158.6	105.6	
100	190.0	180.8	178.6			122.0	48.6	47.8	28.3
75	82.0	80.4				34.5		11.3	

[a]Values in revolutions per minute.

[b]In sequence of application.

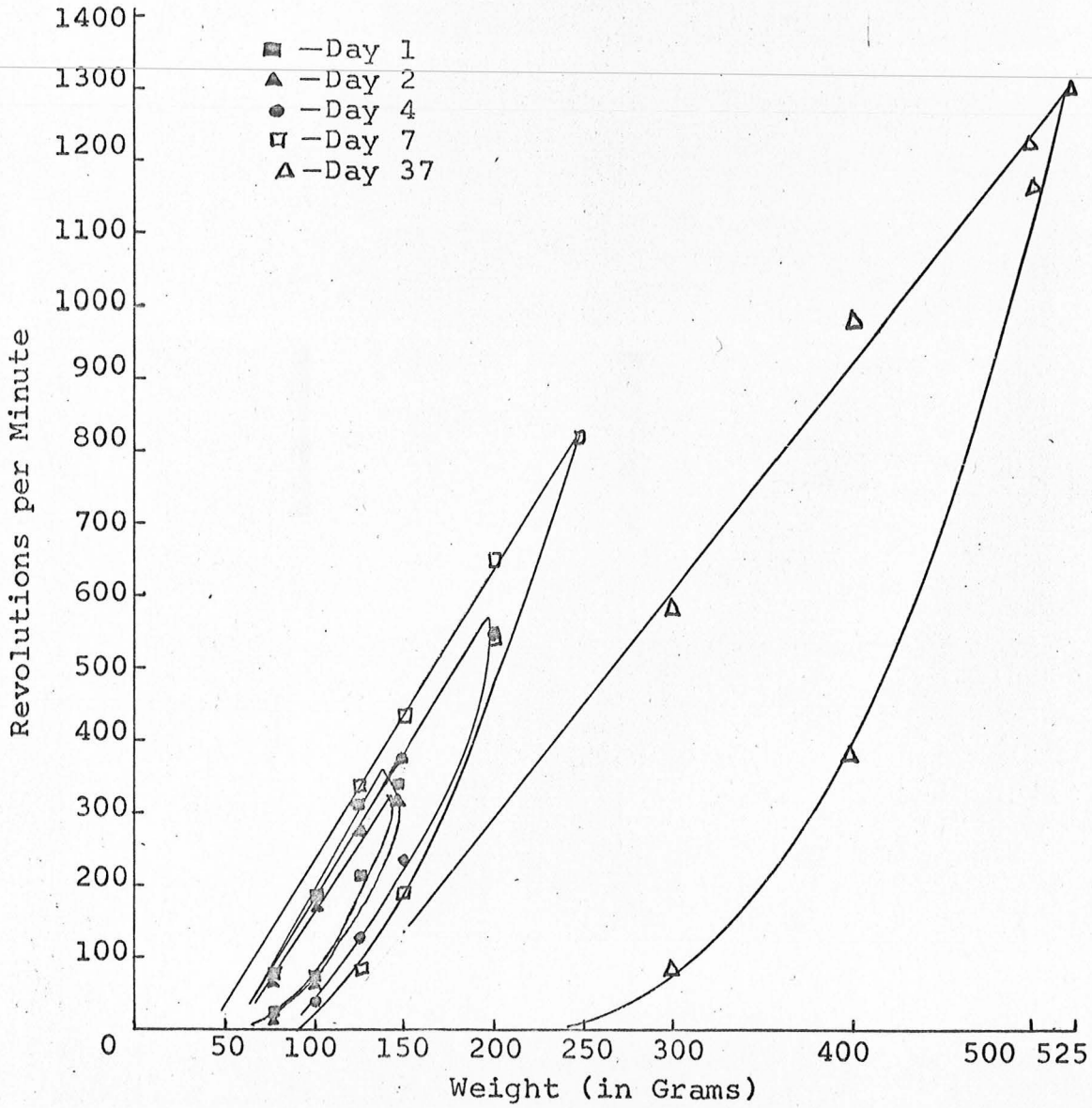

Figure 16. Stormer Viscometer Results of Study on Aging Veegum Samples Stored at Room Temperature. Tested at 25° C.

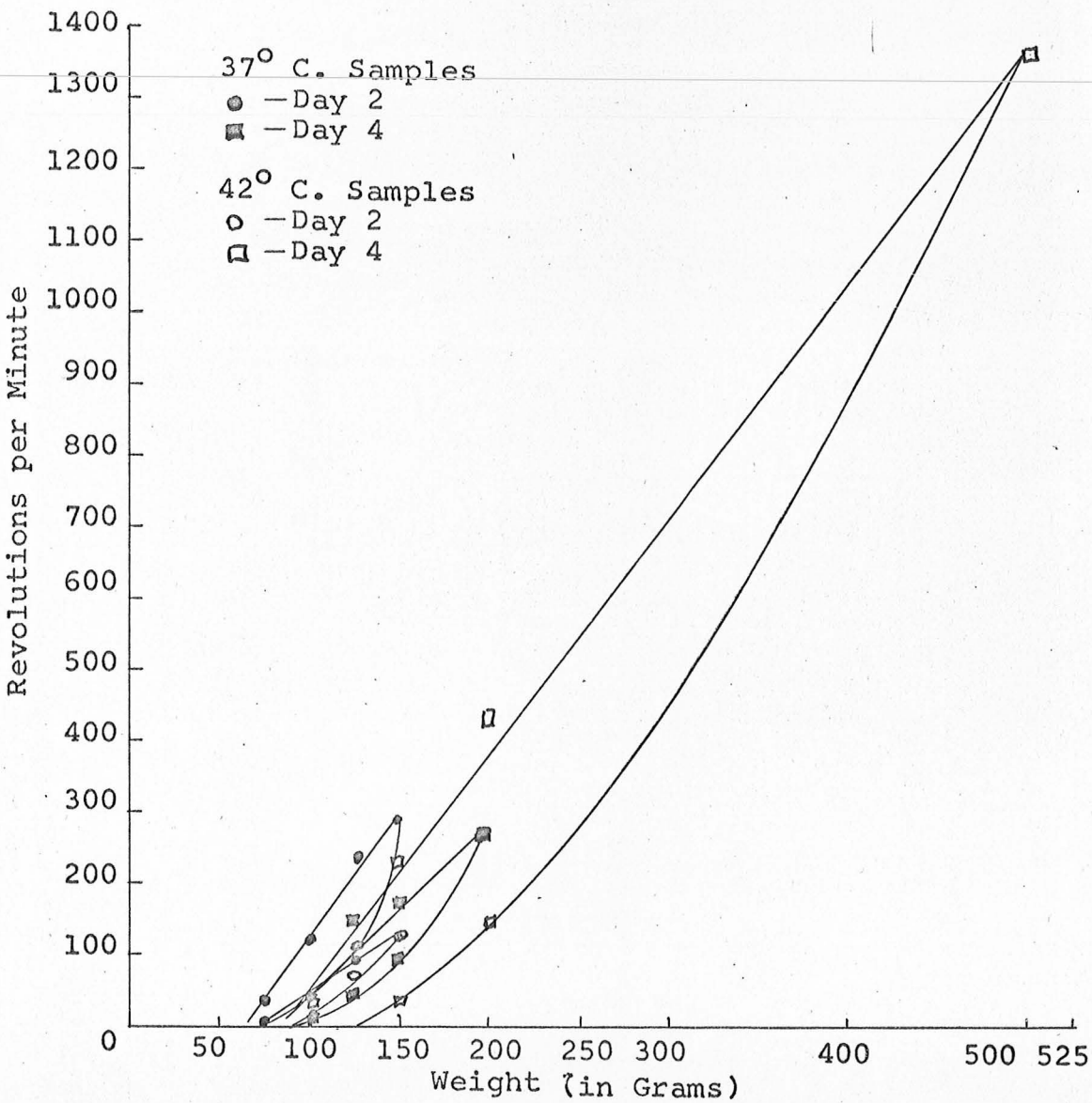

Figure 17. Stormer Viscometer Results of Study on Aging Veegum Samples Stored at 37° C. and 42° C. Tested at 25° C.

Table 6. Brookfield LVT Viscometer Results[a]

Temperature:	Room					37° C.		42° C.	
Day[b] / RPM	1	2	4	7	37	2	4	2	4
0.3	13.3	11.2	12.0	14.4	51.6	18.2	17.4	14.0	23.0
0.6	13.4	10.7	12.0	15.4	50.2	18.5	19.5	15.0	23.7
1.5	13.1	10.7	12.6	16.0	49.5	16.3	19.2	13.5	23.6
3.0	12.9	10.4	12.5	15.3	49.7	16.0	18.0	12.5	22.2
6.0		10.7	12.5	15.3	51.1	15.5	17.5	12.0	22.0
12.0	13.4	11.5	12.6	15.7	55.0	16.0	18.0	11.5	22.0
30.0	15.9	15.0	16.6	16.6	59.2	20.0	20.0	17.0	23.5
60.0	16.1	15.2	16.8	17.2	63.0	20.6	19.0	16.0	23.5
30.0	14.1	13.5	13.7	15.0	53.9	19.0	17.5	16.0	21.0
12.0	11.0	10.5	12.0	13.2	47.8	15.0	16.0	12.0	18.5
6.0	10.1	9.0	10.5	12.1	45.7	13.0	17.0	9.8	16.0
3.0	9.6	8.2	10.0	11.9	43.6	11.5	13.5	10.2	14.5
1.5	8.9	7.8	9.5	11.2	41.5	11.0	13.5	10.0	13.0
0.6	8.3	6.8	8.4	10.0	40.9	11.0	12.5	10.5	13.0
0.3	7.7	6.8	8.5	10.1	40.7	10.5	12.8	10.0	13.2

[a]Values in Brookfield Dial Units using the Number 4 Spindle.
[b]In sequence of application.

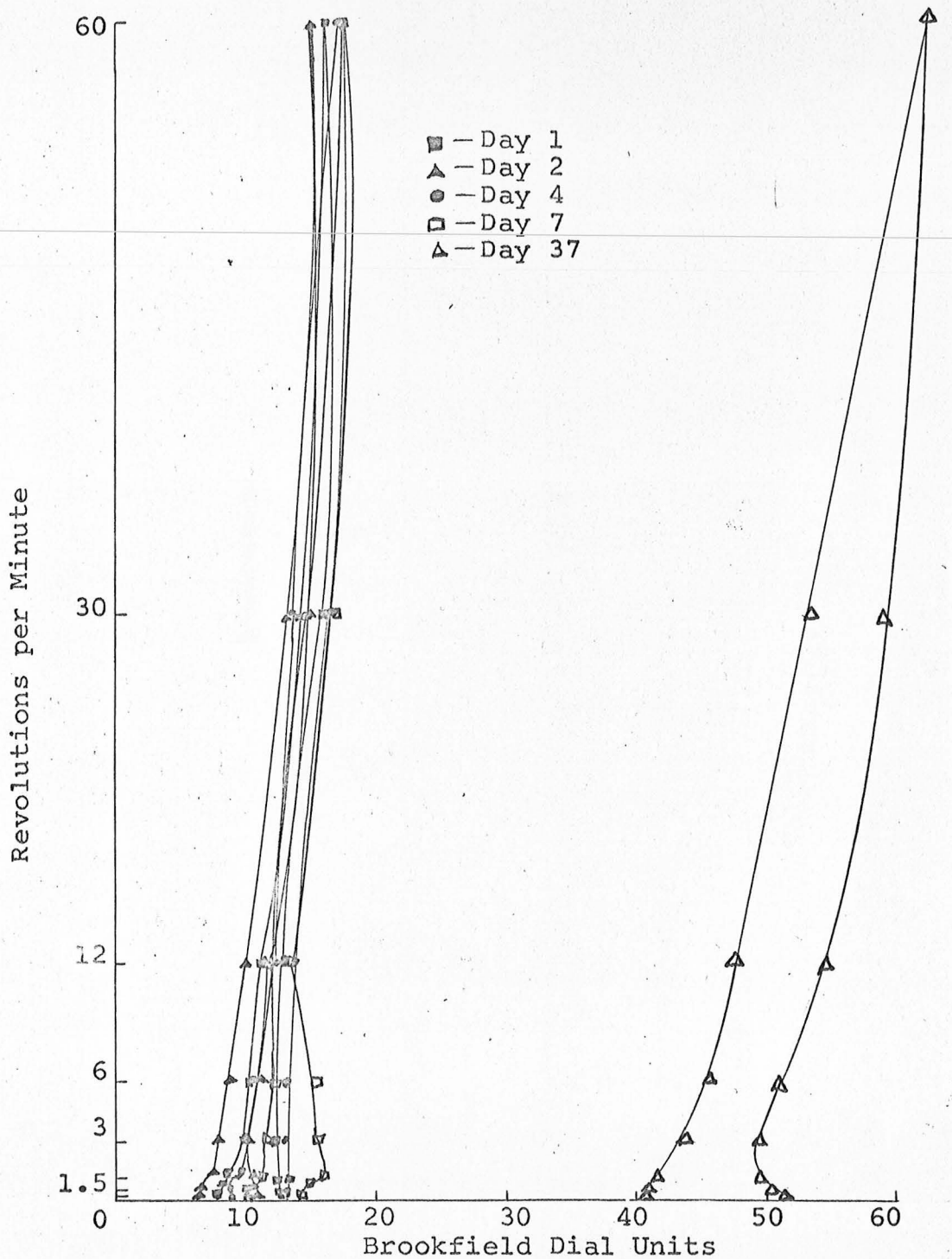

Figure 18. Brookfield LVT Viscometer Results of Study on Aging Veegum Samples Stored at Room Temperature. Tested at 25° C.

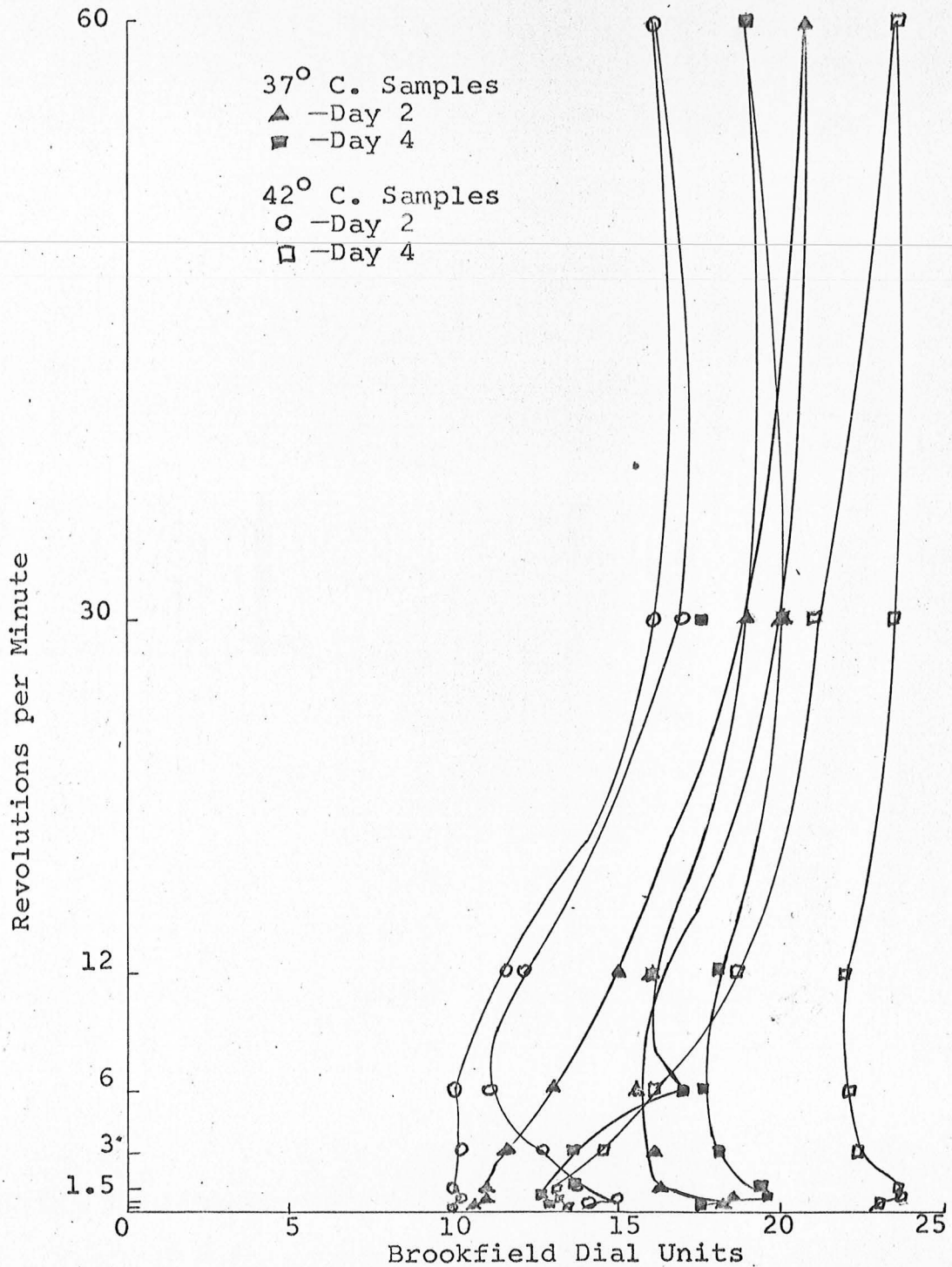

Figure 19. Brookfield LVT Viscometer Results of Study on Aging Veegum Samples Stored at 37° C. and 42° C. Tested at 25° C.

Table 7. Modified MacMichael Viscometer Results[a,b]

Temperature:		Room								37° C.				42° C.			
Day:	1	2		4		7		37[b]		2		4		2		4	
RPM[c]	TU	RPM	TU	RPM	TU	RPM	TU	RPM	TU	RPM	TU	RPM	TU	RPM	TU	RPM	TU
8.7	39.0	9.8	40.3	9.0	31.3	7.1	56.0	16.2	41.7	9.8	40.0	9.0	35.5	9.8	44.8	9.0	56.3
20.1	19.7	20.2	27.3	20.8	17.5	20.0	37.7	26.5	22.3	20.2	25.2	20.8	18.3	20.2	29.2	20.8	37.0
28.7	26.7	29.5	26.3	30.0	16.3	27.3	38.7	35.3	20.2	29.5	25.7	30.0	18.3	29.5	29.4	30.0	25.5
36.2	31.3	36.2	29.8	44.7	17.7	38.0	41.7	38.5	24.4	36.2	26.8	44.7	16.2	36.2	27.2	44.7	20.5
43.2	26.3	44.2	27.3	47.2	19.0	44.3	40.3	39.0	18.0	44.2	26.2	47.2	16.7	44.2	27.4	47.2	20.8
46.8	26.6	47.0	25.7	47.2	16.0	47.0	45.7	38.8	18.0	47.0	25.3	47.2	17.3	47.0	27.8	47.2	21.5
44.8	24.3	44.2	25.2	45.7	13.7	45.3	42.3	38.8	19.0	44.2	23.7	45.7	15.3	44.2	25.8	45.7	20.0
37.6	27.0	36.2	26.3	39.0	13.2	37.7	37.7	38.2	17.8	36.2	23.7	39.0	14.0	36.2	24.0	39.0	16.4
29.6	19.7	29.5	21.7	30.3	12.0	29.7	34.0	35.3	18.0	29.5	21.4	30.3	13.0	29.5	23.8	30.3	20.0
21.5	13.5	20.2	17.2	21.8	10.0	20.0	18.0	25.9	17.5	20.2	15.8	21.8	9.0	20.2	20.0	21.8	14.7
10.7	10.0	9.8	11.0	10.8	7.2	8.0	9.3	17.0	11.5	9.8	12.8	10.8	7.3	9.8	15.4	10.8	13.0

[a]Values in Torque Units using a Pin Setting of 5/8 inch radius.

[b]All readings with the No. 30 torsion wire, except Day 37 using the No. 28 wire.

[c]In sequence of application.

Figure 20. Examples of Results Obtained with the Modified MacMichael Viscometer. Sample Number 2 of the Day 1 Series. Full Scale.

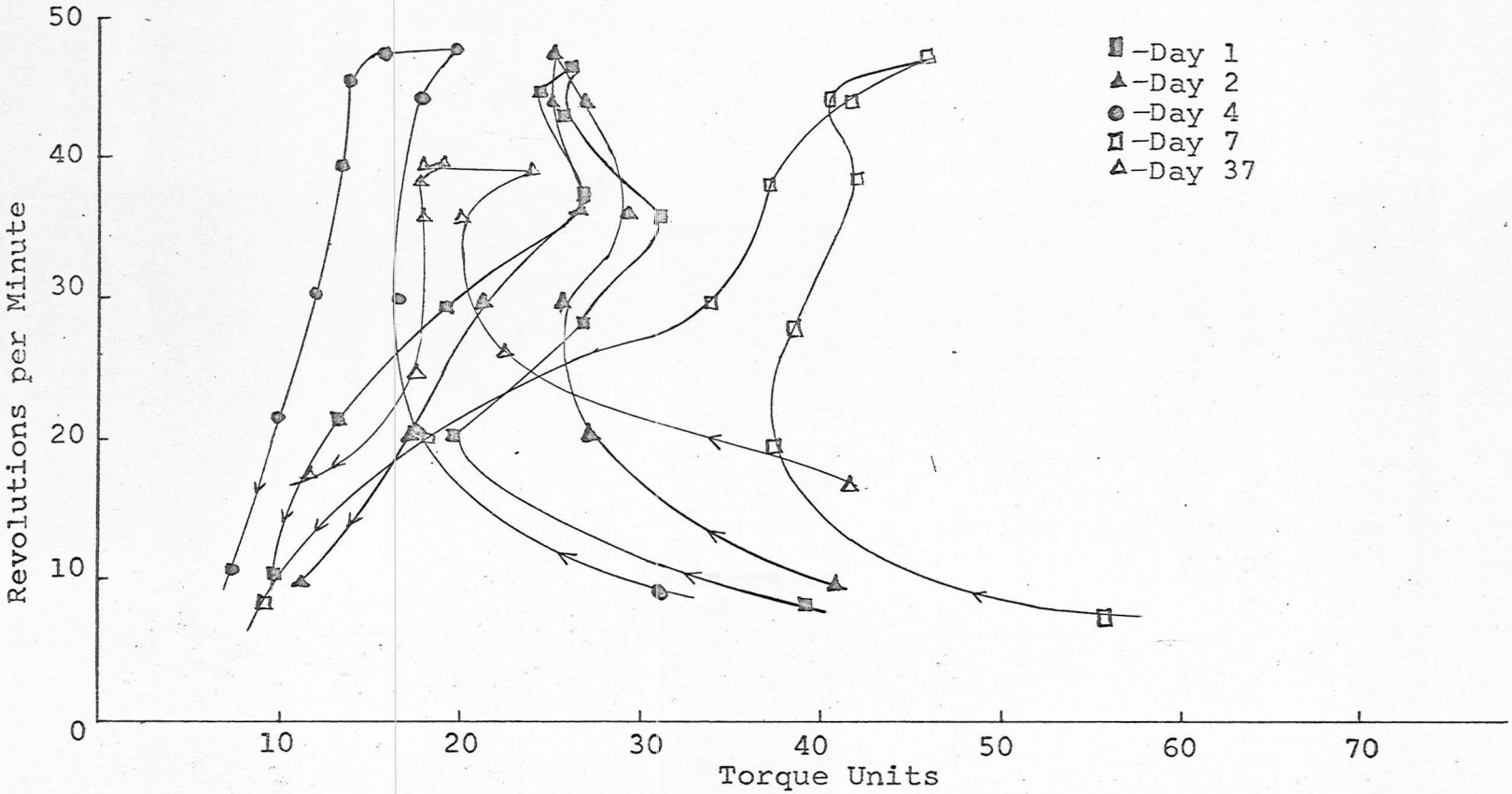

Figure 21. Modified MacMichael Viscometer Results of Study on Aging Veegum Samples Stored at Room Temperature. Tested at 25° C. Number 30 Torsion Wire Used for Days 1 Through 7, and Wire Number 28 Used for Day 37.

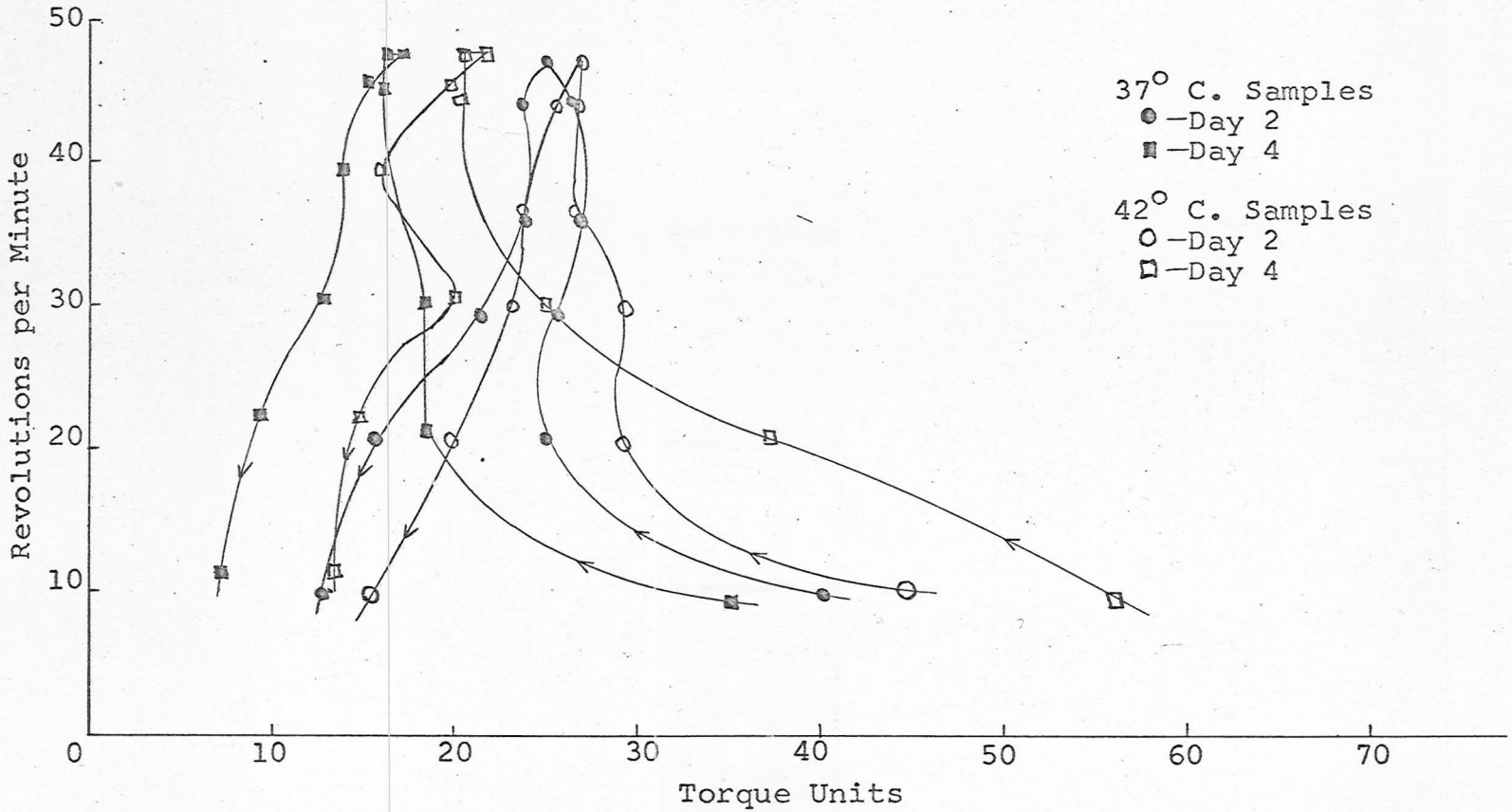

Figure 22. Modified MacMichael Viscometer Results of Study on Aging Veegum Samples Stored at 37° C. and 42° C. Tested at 25° C. Number 30 Torsion Wire Used in All Cases.

C H A P T E R I V

SUMMARY AND CONCLUSIONS

This modified MacMichael viscometer differs from the standard MacMichael viscometer in that it can record continuously throughout the study, and it does not necessitate disruption of the sample prior to testing.

Since two or three ounce ointment jars are used as sample cups, it is possible to store samples for long periods of time prior to study, and there is no need to disturb the sample material by agitation and pouring into a sample cup. It is not necessary to partially destroy the rheologic nature of the sample upon insertion of the bob prior to test, as the pins, which act as test probes, are inserted vertically into the sample. As the pins are raised and lowered vertically into and out of the sample, there are two complete semi-circles of unused material remaining before the test is begun. The new instrument has less friction on the torsion wire than the standard MacMichael viscometer, where the torsion wire may possibly rub against the spindle, and the added viscous material, if glycerin or light mineral oil is added to the dash pot, may alter the observed viscosity of the sample. The shorter torsion wire of the modified MacMichael viscometer is allowed to hang freely into samples of lower viscosity, and a set of ball bearings may be added to the shaft at the bottom of the photoelectric system

support, if necessary for pin alignment in more viscous materials. The modified instrument yields permanent results on the recorder paper, thus providing a continous history of rheologic behavior during examination. It may also be observed from recordings of the Veegum studies that the nature of the material under test can be seen during the first rate of shear test, as seen in Figure 20, and, occasionally, at later stages with Veegum. With the torsion wires used in this study, it is not possible to examine materials of very low viscosity. The 1,005 cp. standard was the lowest viscosity of those examined which would give measurable results. There is the possibility that smaller diameter wires, paddles, or larger diameter pins might be used with materials having lower viscosities. The equipment operated most efficiently with those standards of higher viscosities, as can be seen in the graphs of the standards. Although the actual size of the instrument has not changed appreciably, additional space is required for the recorder, Powerstat and power supply.

All three instruments used in the study gave good linear graphs for the Newtonian standards used. It can be seen from these diagrams that the Stormer viscometer does not appear to be well adapted for high viscosity studies due to the large size weights required. With the torsion wires and pins used here, the modified MacMichael viscometer is not suitable for studies of low viscosity

materials. The Brookfield LVT viscometer appeared to be most effective for the range of standards that were tested. At high rates of shear, the Stormer viscometer will cause the sample to overflow from the sample cup, if the material is of low viscosity. Optical errors are possible when reading the Brookfield LVT viscometer dial, if the experimenter changes his position, or if the rate of shear is high. Errors in timing the one hundred revolutions of the Stormer viscometer are possible when reading the revolutions dial, in delayed reflex action when stopping the stopwatch, and when starting the descension of weights. The modified MacMichael viscometer is less prone to the errors mentioned for the Brookfield LVT and Stormer viscometers, since the results are on the recorder paper and can be thoroughly analyzed after the time of testing. The Brookfield LVT viscometer gives a final reading of viscosity, and the occurrences of rheological breakdown or buildup of material before this time can not be observed. The Stormer viscometer gives an average reading for the time for the weights to descend and cause the bob to rotate one hundred times. As can be observed in Figure 20, the occurrences throughout the time of study with the Modified MacMichael viscometer can be seen on the recorder paper.

In the rheologic examination of the five percent Veegum dispersion, each instrument gives different graphical results of material with the Stormer viscometer producing curves of the nature most commonly described in the

literature of discussions of plastic materials with thixotropy. Figure 20 exhibits the type of results obtained with Veegum on the modified MacMichael viscometer showing thixotropy in runs one and six, but not in run 11 where the material exhibits Newtonian flow. Each instrument exhibits the increasing viscosity yield values for the samples at elevated temperatures. Rheologically, little change is seen through Day 7, while Day 37 samples exhibited greatly increased yield value and thixotropy. These changes are seen best in graphical form. On first observation, the curves of the modified MacMichael viscometer appear to be quite different from those previously reported, however when compared with the Brookfield LVT viscometer results, it can be seen that there is a similarity in the curves. Both begin at the right side and progress to the left side of the graph. The similarity in curve configuration might be even closer, if it were possible to make readings between 30 and 60 revolutions per minute with the Brookfield LVT viscometer. The bob of the Brookfield LVT viscometer, as in the case of the Stormer viscometer, causes considerable disruption of the sample prior to testing, which might account for the closeness of the up-and down-curves with this instrument compared to the greater area under the curve with the modified MacMichael viscometer. Using a shortened Brookfield T-bar in the modified MacMichael viscometer and a regular T-bar in the Brookfield LVT viscometer might produce even

closer results, if a further study were made to compare the instruments.

The picture presented by the modified MacMichael viscometer appears to be more complete than those of the Brookfield LVT and the Stormer viscometers, and it is adaptable to a wide range of rheological studies by changing the torsion wires, pin sizes, pin radius, sample cup sizes, and depth of the pin immersion into the sample. The modified MacMichael viscometer can still be used as originally intended with the spindle and bobs simply by removing the photoelectric system, while retaining the advantage of the top section of the pylon being moveable to raise and lower the bob from and into the sample cup.

Moisture loss from the Veegum samples was shown to be slight, but still present while using regular ointment jar caps, as used here. This will account for some increase in viscosity as the moisture level of the sample decreases. Improved closures should be found before further time studies are attempted.

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